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AN

ELECTROLYTIC STUDY

OF

PYRORACEMIC ACID

THESIS

Presented to the Faculty of the Department of Philosophy of the University of Pennsylvania in partial fulfillment of the requirements, for the degree of Doctor of Philosophy

---

BY

GEORGE WARD ROCKWELL

AKRON, OHIO.

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INTRODUCTION.

It is not necessary to repeat here the various effects of the different oxidizing and reducing agents upon organic compounds, but it may be stated that they do not always produce the same results.

In recent years electrolytic oxygen and electrolytic hydrogen have been brought into use as aids to scientific research in organic chemistry. The effects of these agents upon one organic acid will be discussed in this paper.

It is known that much work has been done in organic electrolysis; further, that the results in very many cases do not give the slightest indication of the conditions under which the experiments were performed. As a consequence of this fact, if attempts are made to repeat the investigations failures to obtain the results frequently follow. Hence it is readily seen that revision is necessarily required in order that proper and reliable conditions may be ascertained.

It has been one of my especial aims to note, as carefully as possible, the conditions under which the work of this research was carried out. They will be given in detail under each experiment.

The possibilities in the oxidation and reduction of pyroracemic acid are briefly these: If boiled with silver oxide it yields carbonic acid and acetic acid, although aldehyde is first formed; if it is heated to 150° C. with dilute sulphuric acid, it breaks down into carbonic acid and acetaldehyde; sodium amalgam or zinc and hydrochloric acid convert it into lactic acid; with hydriodic acid propionic acid is obtained; zinc in contact with an alcoholic solution of the acid changes it to lactic acid and dimethyl tartaric acid. Three of these products, namely, acetic acid, acetaldehyde, lactic acid, and one other, acetic ether, a derivative of acetic acid, I have obtained in its electrolytic oxidation and reduction. Diacetyl might well be expected, and I made numerous attempts to get it, but without result.

APPARATUS.

The apparatus in which the experiments were conducted consisted of a beaker glass, a porous cup, which served as a septum for the separation of the anode and kathode liquids, and two platinum electrodes of 100 sq. c. m. surface. Where hydrochloric acid was used as an electrolyte an anode of carbon was substituted for that of platinum. In several instances lead electrodes were used; these were of the same surface as that of the platinum electrodes.

Whatever substance was used as a conductor in the anode chamber, was also used in the kathode compartment in the form of a 10 to 25 per cent solution.

The solvent generally employed was ordinary alcohol (about 95 per cent). The concentration of the solution electrolyzed depended upon the conditions assumed for each experiment.

When a temperature sufficient to volatilize alcohol was used, a return condenser was inserted into the neck of the porous cup, by means of a large rubber stopper. This also served as a passage for the more volatile aldehyde which was then conducted from the terminal of the condenser tube down through a suitably bent glass tube into ether, chilled by ice water. The aldehyde was precipitated from the ethereal solution by anhydrous ammonia or potassium bisulphite, the latter, however, being very rarely applied.

The current employed in most of the experiments was got from an ordinary 110-volt incandescent light circuit, which was adjusted by means of lamps and wire resistance frames, so that a current ranging from 0.1 to 10 amperes could be used. Sometimes the current from five chloride accumulators, and in one instance only, that of eight gravity cells of the ordinary type was applied.

The temperature was taken with an ordinary thermometer, graduated by the centigrade scale. The readings were made with the thermometer inserted in the kathode liquid.

Attempts were also made to estimate the various products of the electrolysis quantitatively, but I am convinced that they have fallen short in every case. The methods now extant for the estimation of such substances are very unsatisfactory, and in some cases not applicable, as will appear subsequently.

PREPARATION OF PYRORACEMIC ACID.

The method used in the preparation of the pyroracemic acid was that of Emil Erlenmeyer.* It consisted in the dry distillation of tartaric acid with bisulphate of potash.† It might be well to state here that the bisulphate was generally fused before it was used, in order to prevent excessive foaming. The distillate was redistilled under diminished pressure and thus prepared was deemed sufficiently pure for the purpose of the research.

EXPERIMENTAL PART I.

The experiments considered in this part are those in which the oxidizing action of the current was studied.

A. Oxidation in Sodium Hydroxide Solution.

Experiment 1.—This was conducted with the following conditions:

Pyroracemic acid	5.56 grs.
Sodium Hydroxide	10 grs.
Alcohol	100 c.c.
Temperature	Ordinary
Time	22 hours
Normal Density=N. D_{100}	1.3 amperes
Voltage	$3\frac{2}{3}$ volts

Water sufficient to dissolve the sodium hydroxide was also added.

A Bunsen voltameter containing alkali was inserted in the circuit, in order to compare the volumes of the electrolytic and experimental gases given off in the same period of time.

*Berichte 14, 321.

†For the preparation of the greater part of the crude acid I am indebted to my fellow students in the John Harrison Laboratory.

One comparison was made and the experimental gas analyzed. The results of the analysis are as follows:

Volumes of the gases disengaged in the same time:

Electrolytic . . . . . 79.1 c.c.
Experimental . . . . . 12.4 c.c.

The experimental gases were { .4 c.c. CO_2 / 2.8 c.c. O / 9.2 c.c. N }

This analysis shows the presence of air and as the experimental gases evidently did not escape fast enough to prevent the air from entering in at the joints of the apparatus during the time of their collection, no more comparisons were made.

Toward the close of the experiment it was noticed that the brilliancy of the incandescent lamps, through which the current was conducted, was greatly diminished, until finally the filaments became dull red in color. This indicated that the solution in the porous cup had become greatly deficient in its power of conductivity, but the real cause of this behavior was not noticed at the moment.

The contents of the porous cup were poured into a beaker glass, where they were discovered to have changed color, passing from a straw yellow to a cherry red. The solution was allowed to stand over night and then was filtered through a coarse filter paper to remove silica, after which it was distilled over a free flame. The distillate possessed an ethereal odor.

Experiment 2.—The oxidation was made with—

Pyroracemic acid . . . . . 4.33 grs.
Sodium Hydroxide . . . . . 5 grs.
Alcohol . . . . . 50 c.c.
Time . . . . . 5½ hours
Temperature . . . . . Ordinary
N. D_{100} . . . . . 1.3 amperes
Voltage . . . . . 3⅛ volts

Water sufficient to dissolve the sodium hydroxide was also added.

In this experiment the experimental gas was collected after the current had been allowed to act for some time. It was analyzed with the following results:

100 c.c. of gas being taken as sample each time:

Analysis I.

100 c.c. of gas taken during first and second hours:

Carbon dioxide	24.6 c.c.
Oxygen	9.6 c.c.
Carbonic oxide	14.6 c.c.
Nitrogen	51.2 c.c.

Analysis II.

100 c.c. of gas taken during third and fourth hours:

Carbon dioxide	73.2 c.c.

Analysis III.

100 c.c. of gas taken during fourth and fifth hours:

Carbon dioxide	59.6 c.c.
Oxygen	9.4 c.c.
Carbonic oxide	13.6 c.c.
Nitrogen	17.4 c.c.

These gas analyses show that the action of the current had taken effect, either in oxidizing some of the carbon of the pyroracemic acid to carbonic acid, or that it had caused a rupture in the molecule CH_3 CO COOH splitting off carbonic acid.

The contents of the porous cup were treated as above, and it was noticed at this juncture, that the distillate possessed the odor of acetic ether.

Experiment 3.—About twenty-nine grams of pyroracemic acid were used; all the other conditions were not noted, the object being to get a better insight into the gases by a

more rapid evolution of the same from the experimental cell.

Here again the gases were collected in samples of 100 c. c. after the current had acted for several hours.

Analysis I.

Carbon dioxide	92.8 c.c.
Oxygen	3. c.c.
Carbonic oxide	1. c.c.
Nitrogen	3.2 c.c.

Analysis II.

Carbon dioxide	85. c.c.
Oxygen	7.8 c.c.
Carbonic oxide	2.8 c.c.
Nitrogen	4.4 c.c.

The samples for these analyses were collected several hours apart and show conclusively that the action of the current had either caused an oxidation or a breaking down in the molecule of the pyroracemic acid.

The electrolyte in this experiment possessed the color and odor as previously observed.

Experiment 4.—Here the conditions were:

Pyroracemic acid	19.87 grams.
Sodium hydroxide	40. grams.
Alcohol	150 c.c.
Water	100 c.c.
Temperature	Ordinary.
Time	90 hours.
$N.D._{100}$	1.3 amperes.
Voltage	3–4 volts.

Thus far I had collected the gases escaping from the experimental cell over the same water, and I observed that the latter possessed an odor characteristic of aldehyde.

The electrolyte, also, if noticed carefully, was found to bear an aldehydic odor, besides that of acetic ether and alcohol.

As a consequence of these observations, an Erlenmeyer flask containing ether was inserted into the exit tube leading to the vessel in which the water was contained, and allowed to remain for several hours; after which the flask was removed and dry ammonia gas passed through the ether. A white precipitate of aldehyde ammonia was the result. This part of the experiment occurred on the second day.

The electrolyte was poured into a beaker glass and it showed a gray color. It was filtered and distilled, but no compound with a definite boiling point was observed.

The ether used in this experiment was cooled only by a little water drawn from the spigot in an evaporating dish.

Experiment 5.—

Under this head several experiments with varying quantities of pyroracemic acid and sodium hydroxide may be considered. Periods of four, six and eight hours were allowed for the oxidation, and the escaping gases passed through ether cooled as above; but upon the introduction of dry ammonia gas into these several portions of ether the presence of aldehyde was not shown by a white precipitate. In other words, the conditions followed in these experiments were not favorable to the formation of aldehyde, at least in sufficient quantity to be detected in this manner.

The electrolytes being acid, were extracted with ether; the ether distilled off and the residual liquid again distilled. This residual liquid had an ethereal odor at all times, but owing to the presence of large quantities of alcohol, the acetic ether present only in small quantities could not be separated by distillation very well because of the slight difference in the boiling points of the ether and

the alcohol. This difference is exactly one degree centigrade.

Experiment 6.—I here used—

Pyroracemic acid	10 grs.
Sodium Hydroxide	20 grs.
Alcohol	100 c.c.
Water	100 c.c.
Temperature	Ordinary.
Time	6 hours.
N. $D._{100}$	2.6 amperes.
Voltage	6 volts.

A sample of the escaping gas was analyzed; 100 c.c. of it gave—

Carbon dioxide	58.2 c.c.
Oxygen	8 c.c.
Carbonic oxide	1.8 c.c.

The anode liquid was filtered to free it from a slimy precipitate; then it was acidulated with dilute sulphuric acid, which caused a violent effervescence. (Probably due to the absorption of carbon dioxide by the sodium hydroxide.) The liquid then separated into two layers, the upper a reddish brown, the lower a yellow.

The upper layer was drawn off by means of a separatory funnel and extracted with chloroform; the latter was distilled off and the residue appeared to be nothing but tarry decomposition products, with the exception of a small distillate which had a pyroligneous odor but no definite boiling point.

The lower layer was set aside. In a short time it crystallized out. The substance on ignition gave up its water, and this also, by simply drying in the air. Upon testing the amorphous powder left by these processes, it proved to be sodium sulphate.

The precipitate first mentioned was ignited on a platinum foil and afterwards tested for silica. This it proved to be; it having been disintegrated from the porous cup by the action of the sodium hydroxide.

Experiment 7.—The quantities of the materials were:

Pyroracemic acid	5 grs.
Sodium Hydroxide	10 grs.
Alcohol	75 c.c.
Water	50 c.c.
Temperature	33° C.
Time	9 hours.
N. $D._{100}$	1.2 amperes.
Voltage	5 volts.

The escaping gas was analyzed twice for carbon dioxide only. The results were the same for both analyses of samples of 100 c.c. of the gas.

Analysis I.

Carbon dioxide . . . . . 30 c.c.

Analysis II.

Carbon dioxide . . . . . 30 c.c.

The anode liquid was treated as in Experiment 6; it reacted the same.

The upper layer was treated with baric chloride to remove the sulphuric acid; and again with a little sulphuric acid to remove the excess of the baric chloride. The resulting liquid did not show the ordinary test for acetic acid.

Experiment 8.—The following material was used:

Pyroracemic acid	10 grs.
Sodium hydroxide	10 grs.
Alcohol	100 c.c.
Water	85 c.c.
Temperature	30° C.
Time	26 hours.
N.$D._{100}$	1.3–1.1 amperes.
Voltage	4–17 volts.

The exuding gases were passed through ether as above, and upon passing dry ammonia gas into the solution, aldehyde ammonia was once again precipitated. This was the first time I noticed it otherwise than by its odor, after the execution of Experiment 4.

The anode liquid was poured upon a filter from the porous cup, and in performing this operation a violent effervescence was occasioned. The filtrate upon examination was acid to litmus paper. This acid liquid, when coming in contact with the sodium carbonate formed by the absorption of the carbon dioxide by the sodium hydroxide present, caused the evolution of the carbon dioxide just mentioned.

The aldehyde ammonia was now brought upon a weighed filter, washed with ether, dried at the ordinary temperature and weighed. It equaled .0927 grams, or .0648 grams of aldehyde. Calculated as per cent of the theoretical yield, according to the equation: $CH_3\ CO\ COOH = CH_3\ CHO + CO_2$ I obtained only 1.29 per cent of the theoretical yield.

Experiment 9.—The amounts of material varied but little from those in the preceding experiments—

Pyroracemic acid	10	grs.
Sodium hydroxide	10	grs.
Alcohol	100	c.c.
Water	85	c.c.
Temperature	30°–80°	C.
Time	8	hours.
$N.D._{100}$	2.5	amperes.
Voltage	6–20	volts.

With the anode liquid made up as above indicated, the experiment was started and allowed to continue until it became almost a non-conductor, as observed in some of the preceding experiments. The temperature and voltage increased while the amperage naturally decreased.

The gases were passed through ether, as before, and the aldehyde precipitated out by ammonia as above. The yield in this experiment was equal to 0.9656 grams aldehyde, or 19 per cent of the theoretical.

The anode liquids of this and of the preceding experiment were shaken out with ether, which was then evaporated and the residual liquids distilled, but they revealed nothing of definite boiling point. The odors above spoken of were very noticeable in each case.

Here it might be the proper place to offer some theoretical explanation of the reactions so far observed.

First, it seems that aldehyde is the first product of the oxidation, and it appears to be formed by the breaking down of the acid molecule in this manner:

$$CH_3\ CO\ COOH = CH_3\ CHO + CO_2.$$

Secondly, from the very characteristic odor of acetic ether, which is, without a doubt, present, I conclude that it must be formed from the acetic acid, which would naturally be the next product of the oxidation, and the alcohol present in the solution thus:

$$CH_3\ CHO + O = CH_3\ COOH,$$

$$CH_3\ COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O.$$

The singular fact about this is that these reactions took place in a solution, that was strongly alkaline to begin with. But as we know that such ethers are generally formed in acid solutions, the presence of acetic ether here gives very reliable evidence of the formation of acetic acid as a second product.

Thirdly, another reaction, in all probability, takes place thus:

$$CH_3\ COO\ C_2H_5 + NaOH = CH_3\ COO\ Na + C_2H_5OH.$$

By this reaction sodium acetate would be formed, regenerating the alcohol.

All these reactions, of course, are only of theoretical interest.

Experiment 10.—The material used was:

Pyroracemic acid	10 grs.
Sodium hydroxide	10 grs.
Alcohol	100 c.c.
Water	110 c.c.
Temperature	60°–80° C.
Time	5 hours.
N. D_{100}	2.5 amperes.
Voltage	6–56 volts.

The cell containing this solution was placed upon a water bath and was attached to a return condenser, which served to condense any vaporized alcohol. A low flame was applied to keep the temperature within the limits given.

A long glass tube connected the top of the condenser with two Erlenmeyer flasks, which contained anhydrous ether. This tube served to conduct the exuding gases through the ether.

The experiment was interrupted when the bubbles passed slowly through the ether and in place of the return condenser an ordinary Liebig condenser was attached to the anode chamber and the experiment continued. A liquid very like acetic ether in odor began to distil over at 76°–77°C., but almost immediately the temperature rose to 78°C, when alcohol came over. The distillate was collected for several minutes and it had all the appearance and odor of those residual liquids obtained from those ether extractions in the previous experiments.

Here it was learned that alkali heated with aldehyde in alcoholic solution gave a reddish brown coloration. Hence the change in the color in the anode liquid, above noted, can be ascribed to this.

The precipitated aldehyde ammonia in this case equaled 0.7980 grams; equivalent to 0.5755 grams of aldehyde, or one-tenth of the theoretical yield.

The anode liquid was evaporated on the water bath after filteration, when it gave a tarry residue, from which nothing could be sublimed.

Experiment 11.—The same conditions were observed as given above for Experiment 10, with the exception of the time, which was cut down to four hours and twenty minutes. In this experiment the ether was chilled by ice water and a copious precipitate of aldehyde ammonia was obtained. It was not weighed.

Experiment 12.—The conditions were the same as in Experiment 11, only the gases were passed through water, to which a concentrated solution of bisulphite of soda was added, but no addition product was obtained.

Experiment 13.—The conditions were like those of Experiment 12; the gases were passed into ether chilled by ice water, and sodium bisulphite was added. Only a slight amount of the addition product was obtained after the solutions stood three weeks.

Experiment 14.—The conditions were similar to those observed in Experiment 13; after standing for six weeks there was quite a little of the addition product formed. It floated between the layers of the ether and the aqueous bisulphite of soda. Thus it is seen that titration of the aldehyde based on this reaction is almost useless for a solution of this kind.

Experiment 15.—Here again the same conditions were observed, but the aldehyde was precipitated by ammonia gas. It equaled 0.8303 grams aldehyde ammonia; equivalent to 0.5980 grams aldehyde or a trifle over one-tenth of the theoretical yield.

Experiment 16.—The thought now entertained was, that if the aldehyde was the first product of the oxidation, might it not be retained in the cell and then by further action of the current be oxidized more completely to acetic acid. This was tried by electrolyzing a solution contained in a cell surrounded by melting ice, with a feeble current.

The materials used were:

Pyroracemic acid	10 grs.
Sodium Hydroxide	10 grs.
Alcohol	100 c.c.
Water	110 c.c.
Temperature	0°–5°C.
Time	13 hours.
N. $D._{100}$	.45 ampere.
Voltage	14–7 volts.

The anode liquid was poured into a beaker glass and a bulky precipitate was noticed. This was filtered off and dried; upon examination it proved to be sodium carbonate and silica. The filtrate was extracted with ether but showed only such results as those mentioned above.

Experiment 17.—Here I used the following:

Pyroracemic acid	10 grs.
Alcohol	100 c.c.
Temperature	20° C.
Time	1 hour.
$N.D_{100}$	.32 ampere.
Voltage	30–96 volts.

The thought here was to try for the production of acetic acid without the addition of sodium hydroxide. In one hour the anode liquid became a non-conductor and the voltage rose from 30 to 96 volts. This was probably due to the formation of the ethyl ester of pyroracemic acid, as a peculiar ethereal odor was quite noticeable.

Experiment 18.—This was performed according to the conditions under Experiment 10. A better yield of aldehyde was obtained. The aldehyde ammonia equaled 4.88 grams, equivalent to 3.41 grams of aldehyde, or about three-fifths of the theoretical.

Experiment 19.—The conditions were the same as under Experiment 18. Another suggestion was here tried. It being thought that possibly the carbon dioxide might be estimated at the same time with the aldehyde. To this end a weighed tube containing soda lime was inserted in the gas exit, just before the first ether bottle, as two were generally employed. True, a part of the carbon dioxide was caught in this manner, but, no doubt, the greater part was held back by the sodium hydroxide.

The carbon dioxide absorbed by the soda-lime equaled 0.599 grams, equivalent to one-tenth of the theoretical.

The aldehyde ammonia equaled 3.36 grams, equivalent to 2.42 grams aldehyde or about two-fifths of the theoretical.

The anode liquor was made strongly acid with dilute sulphuric acid and distilled over a free flame to a syrupy consistency, when nothing came over at 100° C. The distillate was strongly acid to litmus paper, and on the addition of baric chloride no precipitate was produced.

A known quantity of standard sodium hydroxide was run into the distillate and the excess titrated with standard sulphuric acid.

Supposing the only reaction to take place here to be the following:

$$CH_3\,COOH + NaOH = CH_3\,COO\,Na + H_2O,$$

a yield of 1.1388 grams of acetic acid was obtained.

Again if not all of the pyroracemic acid had been decomposed by the action of the current, it might be either in the form of an ester or the free acid, and upon acidulation and subsequent distillation, it would also be found in the distil-

late. Hence it could vitiate the results. Consequently there seems to be no satisfactory way for the determination or separation of the acetic acid from the anode liquid.

Experiment 20.—This experiment was performed with the following:

Pyroracemic acid	10 grs.
Sodium hydroxide	10 grs.
Water	110 c.c.
Alcohol	100 c.c.
Time	7½ hours.
Temperature	50° C.
$N.D._{100}$	1.35–.85 amperes.
Voltage	5–40 volts.

In this experiment lead electrodes were used. It is seen, from the above data regarding amperage and voltage, that the action proceeded along the same line as it does with the platinum electrodes.

The aldehyde was precipitated as aldehyde ammonia, as before; it equaled 1.5522 grams.

The anode liquid possessing the same reddish brown color as before was treated as usual and revealed the same products.

It was thought that the peroxide of lead being formed at the anode might aid in the oxidation, but it seems to have no action.

Experiment 21.—The conditions observed here were similar to those of Experiment 20, with the exception of the temperature, which was raised to 70° C. For the platinum electrodes two carbon electrodes of 45 sq. c.m. were substituted.

This experiment yielded aldehyde upon the usual treatment. It was not weighed because the preceding attempts had been so unsatisfactory.

It was thought that possibly the carbon would produce milder oxidation, by uniting with the oxygen to form an atmosphere of carbon dioxide, and thus retard the oxidation. In this manner it was hoped to form acetyl superoxide, and then have this break down into diacetyl; thus:

1. $\begin{matrix} CH_3\,CO\,COO\,H \\ CH_3\,CO\,COO\,H \end{matrix} + OOO = H_2O + 2\overline{CO_2} + \begin{matrix} CH_3COO \\ | \\ CH_3COO \end{matrix}$

2. $\begin{matrix} CH_3\,COO \\ | \\ CH_3\,COO \end{matrix} + OO = \begin{matrix} CH_3\,CO \\ | \\ CH_3\,CO \end{matrix} + \overline{2O_2}$

As Schall in 1871 claims to have obtained a persulphide of an analagous formula to that given to acetyl superoxide, it seems, reasoning by analogy, that if diacetyl exists at all it should be obtained from pyroracemic acid, if any acid is to yield it, according to the above indicated reactions.

B. Oxidation in Sulphuric Acid Solution.

Experiment 1.—The following material was employed:

Pyroracemic acid	10 grs.
Sulphuric acid (conc.)	20 c.c.
Alcohol	100 c.c.
Temperature	60°–80° C.
Time	4½ hours.
$N.D._{100}$	2.5 amperes.
Voltage	3 volts.

This experiment was conducted in apparatus similar to that employed in the sodium hydroxide solutions. Aldehyde ammonia was precipitated in the usual manner. The anode liquid also had the odor of acetic ether.

Experiment 2.—In this experiment conditions similar to those in Experiment 1 were observed.

The weighed tube containing soda lime was employed but, as in the previous case, the results were wholly unsatisfactory. Only 0.0942 grams carbon dioxide were obtained.

The anode liquid was shaken out with ether and distilled as usual; the resulting distillate was of the same nature as those produced by the experiments made in sodium hydroxide solution. This is a further proof of the production of acetic acid, as here we have the production of acetic ether in acid solution.

In this experiment another method was tried for the estimation of the aldehyde, namely, its oxidation to acetic acid by chromic acid and the subsequent estimation of the excess of chromic acid by the iodine liberated from potassium iodide. The liberated iodine is titrated with sodium thiosulphate. The method is based upon the following reactions:

1. $CH_3\,CHO + \frac{1}{3}K_2\,Cr_2O_7 = CH_3\,COOH.$

2. $3CH_3\,CHO + K_2Cr_2O_7 + 4H_2SO_4 = 3CH_3\,COOH + Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O.$

Or, 1 and 2 can be written as follows:

3. $3CH_3CHO + 2CrO_3 = 3CH_3\,COOH + Cr_2O_3.$

4. $2CrO_3 + 6KI + 6H_2SO_4 = Cr_2\,(SO_4)_3 + 3K_2SO_4 + 3I_2 + 6H_2O.$

5. $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$

By 4 and 5, the iodine is gotten; by 4 and 3, the acetic acid, and subsequently the aldehyde.

Having, as was the case here, an ethereal solution of aldehyde, it was diluted to a definite volume with ether and a small portion taken for the estimation.

Five c.c. were used and known amounts of bichromate of potash and of sulphuric acid were added. The whole was placed in a rather large test tube, firmly secured with a tight fitting rubber stopper. The test tube was then placed in a water bath at the boiling temperature. The result

was that the rubber stopper was blown high in the air by the expansion of the ether.

One c.c. of the ethereal solution of aldehyde was tried in a similar manner, with like results. No more attempts were made to confine these ether vapors. In passing it might be said that such a method might be applicable for the estimation of aldehyde in very dilute alcoholic or aqueous solutions.

Experiment 3.—The following conditions were observed:

Pyroracemic acid	10 grs.
Alcohol	100 c.c.
Sulphuric acid (conc.)	25 c.c.
Temperature	50° C.
Time	27 hours.
N. $D_{\cdot 100}$	0.45 ampere.
Voltage	2⅔ volts.

The thought entertained here was that with low pressure and density there was a possibility of obtaining diacetyl in sulphuric acid solution. No attempt was made to collect the exuding gases. An inverted condenser was used to return any alcohol.

The anode liquor was extracted with ether several times, but nothing new was found.

Experiment 4.—Here I used:

Pyroracemic acid	20 grs.
Alcohol	150 c.c.
Sulphuric acid (conc.)	25 c.c.
Temperature	50° C.
Time	24 hours.
N. $D_{\cdot 100}$	0.45 ampere.
Voltage	3 volts.

The anode liquid treated in the usual way gave nothing new.

Experiment 5.—The conditions in this experiment are the following :

Pyroracemic acid	10 grs.
Sulphuric acid (conc.)	20 c.c.
Alcohol	100 c.c.
Time	7½ hours.
Temperature	60° C.
N. $D_{.100}$	1.4 amperes.
Voltage	4⅓ volts.

Lead electrodes were employed. Aldehyde was precipitated by ammonia, but was not weighed for the reasons already noted.

The anode liquid yielded nothing new.

Experiment 6.—The conditions observed here are similar to those under Experiment 5, with the exceptions of time and density. The time was 3 hours and N. $D_{.100} = .9$ ampere.

Carbon electrodes were used. Aldehyde and the other products were obtained as usual. This experiment was interrupted at the point when it was supposed that the aldehyde would begin to come off, but such a point was not found.

C. Oxidation in Hydrochloric Acid Solution.

Experiment 1.—The following conditions were observed :

Pyroracemic acid	10 grs.
Hydrochloric acid (conc.)	30 c.c.
Alcohol	100 c.c.
Time	5 hours.
Temperature	60°–70° C.
N. $D_{.100}$	2.5 amperes.
Voltage	5 volts.

A carbon plate was substituted for the platinum anode in these experiments, otherwise they were conducted as those which precede them.

Upon the passage of ammonia gas into the chilled ether a white coloration was produced, but it disappeared after a short time. This was probably due to a little volatilized hydrochloric acid gas in the ether, or perhaps there was sufficient water in the ether to dissolve it.

The anode liquid was treated as above, but gave nothing other than what had been noted previously.

Experiment 2.—Here I used:

Pyroracemic acid	20 grs.
Hydrochloric acid (conc.)	60 c.c.
Alcohol	150 c.c.
Time	24 hours.
Temperature	50° C.
$N.D._{100}$	0.4 ampere.
Voltage	18 volts.

The anode in this experiment was a common graphite pencil with the wood removed at both ends.

My hope was that I might obtain diacetyl, but without avail.

Experiment 3.—Material slightly varied again:

Pyroracemic acid	20 grs.
Alcohol	100 c.c.
Hydrochloric acid (conc.)	30 c.c.
Temperature	40° C.
Time	10 hours.
$N.D._{100}$	1.35 amperes.
Voltage	5 volts.

A carbon plate was used here.

The anode liquid, analyzed as before, revealed nothing new.

D. Oxidation of Certain Salts of Pyroracemic Acid.

Experiment 1.—The magnesium salt was employed here; as the calcium salt of pyroracemic acid is crystalline, and as no record is seen of the magnesium salt an attempt was made to get it in a crystalline form.

The acid was first neutralized in aqueous solution with magnesium oxide and evaporated down, but the salt did not crystallize. The carbonate of magnesium was next tried, and the solution divided into two parts, one being allowed to evaporate in the air, the other over sulphuric acid in a vacuum desiccator. Neither, however, produced a crystalline salt, although they were allowed to stand more than a month. At the expiration of that time the solutions were evaporated to dryness in the water bath ; a gummy looking, but very brittle and fragile substance was obtained. In color it was a dirty brown.

Two experiments were tried with this salt dissolved in water, but unfortunately each time, for some unknown reason, the porous cup, in which the solutions were contained, was floated on the top of the kathode liquid at the end of one hour in each case. As a consequence of this nothing more can be said in regard to it.

Experiment 2.—The sodium salt was used here. The salt was obtained by the solution of the carbonate of sodium and subsequent evaporation. The material employed was:

Sodium pyroracemate	10 grs.
Alcohol	50 c.c.
Water	100 c.c.
Time	7 hours.
Temperature	25°–40° C.
$N.D._{100}$	0.45–.2 ampere.
Voltage	9–58 volts.

Platinum electrodes were used.

The anode liquid possessed an aldehydic odor and had the usual reddish brown color. It was shaken out with ether and treated as before, as the solution was acid.

These salts were prepared and electrolyzed to produce diacetyl if possible, but no indications of it were noticed.

The kathode liquid in this case was sodium hydroxide.

Experiment 3.—The sodium salt was again electrolyzed with conditions similar to those of Experiment 2, excepting those of voltage and amperage. These were:

Voltage	20–60 volts.
$N.D._{100}$	1.1–.5 amperes.

These changes, however, affected the general course of the experiment in no way.

Experiment 4.—The iron salt was used here. It was obtained by the solution of ferric oxide and subsequent evaporation. It is a brittle substance. Sodium hydroxide was added to increase its conductivity.

The material employed here was:

Iron pyroracemate	5 grs.
Water	75 c.c.
Alcohol	50 c.c.
Sodium hydroxide	2.5 grs.
Temperature	30° C.
Time	7 hours.
$N.D._{100}$	.4 amperes.
Voltage	10 volts.

The electrodes were of platinum and the kathode liquid sodium hydroxide.

The anode liquid was acid, and was shaken out with ether; in the resulting distillate no signs of diacetyl were observed.

Experiment 5.—The iron salt was again electrolyzed with a higher current, the other conditions being similar to those of Experiment 4.

$N.D._{100}$	1.3 amperes.
Voltage	9-70 volts.
Time	5 hours.

The anode liquid possessed a strong odor of aldehyde, but revealed nothing else.

E. Oxidation in Sodium Carbonate Solution.

Experiment 1.—Here I used the following:

Pyroracemic acid	10 grs.
Time	6 hours.
Temperature	30° C.
$N.D._{100}$	1.35 amperes.
Voltage	6 volts.

The pyroracemic acid was dissolved in 100 c. c. of water and neutralized with sodium carbonate. The kathode liquid was also a solution of sodium carbonate.

It was found that after a time the anode liquid became acid. The escaping gases were tested for carbon dioxide and found to contain 93 per cent. This indicates action similar to that produced in a sodium hydroxide solution.

Experiment 2.—Observing that no diacetyl had as yet been obtained, it was suggested to keep the anode liquid perfectly alkaline by means of sodium carbonate added from time to time; also to keep the kathode liquid as nearly neutral as possible by running a stream of carbon dioxide into the same. With these precautions all of the following experiments were directed to the formation of diacetyl.

In this experiment the following were used:

Pyroracemic acid	20 grs.
Time	9½ hours.
Temperature	30° C.
$N.D._{100}$	1.35 amperes.
Voltage	6 volts.

The pyroracemic acid was dissolved in 100 c.c of water and neutralized with sodium carbonate. A small addition of the same was made every half hour. The anode liquid was taken out and distilled over a free flame. The distillate was salted out with common salt and re-distilled. This procedure gave a greenish yellow distillate, very like the color of diacetyl. This was dehydrated over calcium chloride and distilled again. It retained the same color, but the odor was very like that of a weak solution of the pyroracemic acid itself, after being boiled.

The boiling point of diacetyl (87–88° C.) was never approached in the distillation of this substance.

Experiment 3.—Here I used:

Pyroracemic acid	50 grs.
Water	100 c.c.
Time	12 hours.
Temperature	30° C.
$N.D._{100}$	1.3 amperes.
Voltage	5–6 volts.

This experiment was conducted like Experiment 2, with the hope of obtaining more of such a mixture, but apparently the distillate was as dilute as in the other instance.

Experiment 4.—The following were used:

Pyroracemic acid	20 grs.
Water	100 c.c.
Time	9 hours.
Temperature	30° C.
$N.D._{100}$	.85 ampere.
Voltage	10 volts.

This experiment was conducted like experiments 2 and 3. When the anode liquid was distilled it gave a lighter colored distillate, with a weaker odor.

Experiment 5.—Again I employed the following :

Pyroracemic acid	20 grs.
Water	100 c.c.
Time	10 hours.
Temperature	30° C.
$N.D._{100}$	1.8 amperes.
Voltage	10 volts.

The anode liquor was acidulated with dilute sulphuric acid and then distilled ; the distillate salted out as before and redistilled. It gave a greenish yellow distillate, which was treated according to the method of Peckmann.* In accordance with this, normal potassium hydroxide was added to the solution to alkaline reaction, but it did not become colorless or a faint brown as Peckmann asserts. It, however, became a light yellow in color. It was then acidulated with dilute sulphuric acid and extracted several times with ether. The ether was distilled off and a yellowish green substance was left instead of a colorless oil as directed.

The object of this treatment was to form if possible the aldol of diacetyl, which has the following constitution :

$$CH_3\ CO\ COH\ CH_2\ CO\ CO\ CH_3.$$

From what I obtained from the ether extractions, I attempted to produce p-xyloquinone, by treatment with potassium hydroxide, which would constitute a conclusive test for diacetyl. This, however, was not obtained. The p-xyloquinone has the following constitution :

$$\begin{array}{c} CH_3\ C\ CO\ CH \\ \quad\quad\ \| \quad\quad\ \| \\ CH\ CO\ C\ CH_3 \end{array}$$

It is described as a golden yellow crystalline compound ; crystallizing from alcohol in needles and subliming unde-

*Berichte 28, 1846.

composed. No product of such characteristics appeared in the attempted transformations.

Still laboring under the impression that possibly that greenish yellow material might possibly be the sought for substance, several experiments were tried; some with the same conditions as those given above and others with them slightly different. The anode liquids were all treated as has been described, but no test for diacetyl revealed its presence. The conditions of these experiments will follow in their order.

Experiment 6.—The same conditions were observed as those given in Experiment 5; results similar.

Experiment 7.—Here potassium carbonate was used instead of sodium carbonate, otherwise the same conditions as in Experiment 5 were observed; results as before.

Experiment 8.—Again potassium carbonate was used, and twenty-four hours allowed for duration of this experiment. The distillate in this case was almost colorless.

Experiment 9.—Here I used:

Pyroracemic acid	20 grs.
Temperature	25° C.
Time	20 hours.
Water	100 c.c.
N. $D._{100}$	.1 ampere.
Voltage	3 volts.

The anode liquid thus prepared was neutralized with sodium carbonate and about 20 c.c. of alcohol were added. It was then electrolyzed with a feeble current, which was allowed to run over night. The next day the anode liquid was acid and possessed the odor of acetic ether, and also that of aldehyde. Hence we have these produced in a solution originally alkaline with sodium carbonate.

The current employed was obtained from gravity cells.

Experiment 10.—The same conditions as were used in Experiment 5 were again tried; results again similar.

Experiment 11.—The same conditions as were observed in Experiment 5 were used again, with the exception of voltage and amperage. These were:

Voltage . . . . . 22 volts.
N. D_{100} . . . . . 1.1 amperes.

This, however, seemed to have no influence upon the desired result.

A perusal of this experimental part shows that the conditions were carefully noted, and that the methods employed for the estimation of the products are sadly deficient.

It can, however, be stated with positive certainty that aldehyde, acetic acid, and acetic ether have been made from pyroracemic acid in the electrolytic way.

It is almost useless to attempt to cite the experiments and the conditions, which are the most favorable to the formation of any one of these products, because the analytical results permit of no deductions.

The results, as given, will, if examined carefully, confirm the above statement.

In regard to the formation of diacetyl it seems very probable that if the proper conditions were once found, its formation would be an easy matter.

If the existence of diacetyl were once established it would throw some light on the way in which organic acids undergo decomposition by the action of the electric current. Once isolated it would prove almost with certainty the existence first of a superoxide; and this would do away with the speculation that is now carried on as to the existence of the same.

It can be remarked in passing that similar results were always produced, no matter what the substance used as electrodes was.

EXPERIMENTAL PART II.

In the reduction of pyroracemic acid the porous cup was made the kathode chamber.

A. Reduction in Sodium Hydroxide Solution.

Experiment 1.—The following material was employed:

Pyroracemic acid	5 grs.
Alcohol	50 c.c.
Water	50 c.c.
Sodium hydroxide	8 grs.
Temperature	Ordinary.
Time	7 hours.
$N.D_{100}$	.45 ampere.
Voltage	3⅓ volts.

The kathode liquid was taken out and acidulated with dilute sulphuric acid, then extracted with ether several times. The ether was evaporated and the residual liquid heated in a porcelain dish for some minutes on a water bath to expel any dissolved ether.

These operations were performed according to the directions given in Beilstein's "Organic Chemistry" for the detection and estimation of lactic acid; as were also the subsequent operations which will now follow.

Lead acetate was added to remove any sulphuric acid present. The lead sulphate formed was filtered off and more lead acetate added together with alcoholic ammonia (alcohol 90 per cent, ammonia 10 per cent), until no further precipitation was noticed. A white, slimy precipitate was obtained, which, according to the above-mentioned authority, has the following composition: 3 PbO. $C_3H_6O_3$. This was filtered off, washed with alcohol, dried at 100° C. and weighed. The same writer quotes that this precipitate contains 78.5 per cent PbO., therefore there is 21.5 per cent

free lactic acid contained in it also. The precipitate in this case weighed 2.595 grams, corresponding to .5579 grams of lactic acid.

The theoretical can proceed according to the equation:

$$CH_3\ CO\ COOH + H_2 = CH_3\ CH\ (OH)\ COOH;$$

hence, according to this 10.91 per cent of the theoretical yield was obtained.

Experiment 2.—Here I used:

Pyroracemic acid	5 grs.
Alcohol	75 c.c.
Water	50 c.c.
Sodium hydroxide	10 grs.
Temperature	Ordinary.
Time	5 hours.
$N.D._{100}$	.8 ampere.
Voltage	4 volts.

The kathode liquid was acidulated and treated as above. The precipitate weighed 6.7581 grams, equivalent to 1.4529 grams of lactic acid, and corresponding to 28.43 per cent of the theory.

Experiment 3.—The material was:

Pyroracemic acid	5 grs.
Sodium hydroxide	8 grs.
Alcohol	50 c.c.
Water	50 c.c.
Temperature	50° C.
Time	6 hours.
$N.D._{100}$	.7 ampere.
Voltage	4 volts.

The kathode liquid under the prescribed treatment yielded 3.9592 grams of precipitate, corresponding to 0.8512 grams lactic acid; equivalent to 16.65 per cent of theory.

In these three experiments platinum electrodes were employed.

Experiment 4.—The following were used:

Pyroracemic acid	20 grs.
Sodium hydroxide	10 grs.
Alcohol	100 c.c.
Water	110 c.c.
Temperature	60° C.
Time	5 hours.
$N.D._{100}$	.9 ampere.
Voltage	5–6 volts.

The kathode liquid, treated as usual, gave 4.5860 grams of the lead salt, corresponding to .9859 grams of lactic acid equivalent to 9.64 per cent of theory.

Lead electrodes were used in this experiment.

B. Reduction in Sulphuric Acid Solution.

Experiment 1.—Here I used:

Pyroracemic acid	10 grs.
Alcohol	75 c.c.
Sulphuric acid (conc.)	20 c.c.
Temperature	30° C.
Time	21 hours.
$N.D._{100}$	.45 ampere.
Voltage	3 volts.

The kathode liquid was directly shaken out with ether, as it was an acid solution, otherwise treatment was the same as when an alkaline solution was used.

It yielded 3.0499 grams of the lead salt, corresponding to 0.6557 grams of lactic acid, equivalent to 6.41 per cent of the theory.

Experiment 2.—The following was used:

Pyroracemic acid	10 grs.
Sulphuric acid (conc.)	20 c.c.
Alcohol	75 c.c.
Temperature	30° C.
Time	9 hours.
$N.D._{100}$	.45 ampere.
Voltage	3 volts.

The kathode liquid gave 7.1718 grams of the lead salt, corresponding to 1.5417 grams of lactic acid, equivalent to 15.08 per cent of the theory.

Experiment 3.—Here I used:

Pyroracemic acid	5 grs.
Sulphuric acid (conc.)	20 c.c.
Alcohol	75 c.c.
Temperature	30° C.
Time	6 hours.
$N.D._{100}$	.6 ampere.
Voltage	3⅓ volts.

The usual treatment gave 5.3731 grams of the lead salt, corresponding to 1.1552 grams of lactic acid, equivalent to 22.60 per cent of the theory.

Experiment 4.—Here the following were used:

Pyroracemic acid	5 grs.
Water	50 c.c.
Sulphuric acid (conc.)	25 c.c.
Alcohol	50 c.c.
Time	6 hours.
Temperature	35° C.
$N.D._{100}$	.8 ampere.
Voltage	3⅓ volts.

This yielded 6.4670 grams of the lead salt, corresponding to 1.3904 grams of lactic acid, equivalent to 27.19 per cent of the theory.

Experiment 5.—The following were used here:

Pyroracemic acid	10 grs.
Sulphuric acid (conc.)	50 c.c.
Alcohol	60 c.c.
Temperature	20–30° C.
Time	53 hours.
$N.D._{100}$	.55 ampere.
Voltage	3⅓ volts.

The kathode liquid yielded 4.1243 grams of the lead salt, corresponding to 0.8867 grams of lactic acid, equivalent to 8.67 per cent of the theory.

Experiment 6.—The material used was:

Pyroracemic acid	5 grs.
Sulphuric acid (conc.)	20 c.c.
Alcohol	75 c.c.
Water	25 c.c.
Temperature	50° C.
Time	6 hours.
$N.D._{100}$	.85 ampere.
Voltage	3 volts.

This gave 5.1970 grams of the lead salt, corresponding to 1.1173 grams of lactic acid, equivalent to 21.86 per cent of the theory.

Experiment 7.—Here I used:

Pyroracemic acid	5 grs.
Alcohol	25 c.c.
Sulphuric acid (conc.)	20 c.c.
Water	75 c.c.
Temperature	25° C.
Time	10 hours.
$N. D._{100}$	.83 ampere.
Voltage	3 volts.

The kathode liquid yielded 2.6200 grams of the lead salt, corresponding to 0.5633 grams of lactic acid, equivalent to 11.01 per cent of the theory.

Experiment 8.—The following conditions were observed here:

Pyroracemic acid	10 grs.
Sulphuric acid (conc.)	20 c.c.
Alcohol	75 c.c.
Water	50 c.c.
Temperature	50° C.
Time	6 hours.
N. $D_{\cdot 100}$	.95 ampere.
Voltage	2⅓ volts.

The kathode liquid gave 8.6248 grams of the lead salt, corresponding to 1.8543 grams of lactic acid, equivalent to 18.14 per cent of the theory.

Experiment 9.—The following were used here:

Pyroracemic acid	15 grs.
Alcohol	75 c.c.
Sulphuric acid (conc.)	20 c.c.
Temperature	50° C.
Time	6 hours.
N. $D_{\cdot 100}$	1.5 amperes.
Voltage	3⅓ volts.

The kathode liquid gave 8.8470 grams of the lead salt, corresponding to 1.8921 grams of lactic acid, equivalent to 11.68 per cent of the theory.

In the above mentioned experiments platinum electrodes were used.

Experiment 10.—Lead electrodes were used in the experiment with the following conditions:

Pyroracemic acid	10 grs.
Sulphuric acid (conc.)	10 c.c.
Alcohol	100 c.c.
Temperature	50° C.
Time	4½ hours.
$N.D._{100}$	.85 ampere.
Voltage	5-6 volts.

The yield was 3.3203 grams of the lead salt, corresponding to 0.7138 grams of lactic acid, equivalent to 6.97 per cent of the theory.

Experiment 11.—Carbon electrodes were employed here with the following conditions:

Pyroracemic acid	10 grs.
Sulphuric acid (conc.)	15 c.c.
Alcohol	100 c.c.
Water	50 c.c.
Temperature	60° C.
Time	4½ hours.
$N.D._{45}$	.9 ampere.
Voltage	3.5 volts.

The kathode liquid gave 3.7693 grams of the lead salt, corresponding to 0.8103 grams of lactic acid, equivalent to 7.93 per cent of the theory.

As propionic acid is one of the possibilities of this reduction, it was tested for in the following manner:

The filtrates from several of the above experiments were made acid with hydrochloric acid, and the lead thrown out either as lead chloride or lead sulphide. The solutions were filtered and boiled to remove the hydrogen sulphide, and then neutralized with barium carbonate and again filtered.

They were then evaporated to crystallization.

As acetic acid had been added in the form of lead acetate, it was now present as barium acetate together with the barium propionate, if the latter were present at all. The crystals thus obtained were acidulated with dilute sulphuric acid and distilled, but no boiling point near to that of propionic acid was reached. So the conclusion is that it was not formed in any but small quantities, if formed at all.

In this experimental part as the analytical results are approximate, it might be well to state in conclusion the maximum and the minimum yields of lactic acid.

In alkaline solution under the conditions of experiment (2) the maximum was obtained, while under those of (4) the minimum. The figures are 28.43 and 9.64 per cent of the theoretical yields.

In sulphuric acid solution, under experiment (4), the maximum 27.19 per cent, and under experiment (1), the minimum 6.41 per cent of the theoretical was obtained.

In the reduction of pyroracemic acid by electrolytic hydrogen, it seems natural that lactic acid should be the first product of the reduction ; also, that by further reduction propionic acid should be obtained. Probably it is, but no very definite test can be applied to detect it in such a mixture as that, in which, it would occur here.

It is, in my opinion, formed at least in small quantities and probably if exceedingly large quantities of pyroracemic acid were electrolyzed and treated as described its presence would be found.

Further, it is noticed in this part also, that the change in the kind of electrodes causes no marked difference.

The conditions in this part have also been carefully noted.

APPENDIX.

Oxidation of Lævulinic Acid.

The lævulinic* acid was prepared in the usual manner by treatment of starch with hydrochloric acid. The syrupy liquid was then distilled in a vacuum; the acid thus prepared was deemed sufficiently pure for this purpose.

Experiment 1.

Lævulinic acid	10 grs.
Sulphuric acid (conc.)	20 c.c.
Water	50 c.c.
Alcohol	100 c.c.
Temperature	30° C.
Time	8 hours.
N. $D._{100}$	.9 ampere.
Voltage	2½-3 volts.

Platinum electrodes were employed here.

The anode liquid was extracted with ether and the ether evaporated.

The residual liquid was distilled. The distillate possessed the odor of acetic ether. This was saponified with sodium hydroxide and then a few drops of alcohol were added together with a little sulphuric acid. The same odor was again produced.

Thus it is seen that acetic acid and acetic ether are produced in the electrolysis of lævulinic acid.

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*For the crude acid I am indebted to my fellow student W. C. Ebaugh.

Experiment 2.

A sodium hydroxide solution was used in this experiment.

Lævulinic acid	10 grs.
Sodium hydroxide	10 grs.
Water	50 c.c.
Alcohol	100 c.c.
N. $D_{\cdot 100}$	1.3 amperes.
Voltage	4⅓ volts.
Temperature	30° C.
Time	4½ hours.

The anode liquid was of a dark red color after the action of the current, and possessed an odor very like that of a freshly cut apple. It was acid to litmus.

A little sulphuric acid was added and then it gave off the odor of acetic ether as clearly as did the anode liquid from Experiment 1. Thus I conclude that acetic acid and acetic ether, and probably aldehyde, judging from the color of the anode liquid after the action of the current, are formed in an alkaline solution of lævulinic acid.

Only two experiments were tried, one in alkaline and the other in acid solution. Similar results were obtained in each case, *i. e.*, acetic acid and acetic ether.

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I take this opportunity of expressing my sincere gratitude to Professor Edgar F. Smith for the friendly interest and ever ready suggestion he has offered in the prosecution of this research, in a comparatively new field.